PROCEEDINGS

OF THE

AMERICAN ACADEMY

OF

ARTS AND SCIENCES.

VOL. XVIII.

PAPERS READ BEFORE THE ACADEMY.

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I.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

# ON CERTAIN SUBSTANCES OBTAINED FROM TURMERIC. — II. CURCUMIN.

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Presented May 10th, 1882.

IN the following paper * we have the honor of laying before the Academy a description of our experiments on the action of nascent hydrogen and of bromine upon curcumin.

## *Action of Nascent Hydrogen.*

*Dihydride of Curcumin*, $C_{14}H_{16}O_4$. This substance was made by the action of sodium amalgam and water upon curcumin. The best result was obtained when a mixture of curcumin, dilute alcohol, and strong sodium amalgam was allowed to stand for somewhat more than a week. The alcohol, though not absolutely necessary, as the sodic hydrate formed gradually brings the curcumin into solution, accelerates the action, which at best is extremely slow. After the dark-red color of the sodic salt of curcumin had given place to a blackish tinge, the liquid was poured off from the mercury, acidified with hydro-

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* The first paper was published in these Proceedings, Vol. XVII. p. 110.

chloric acid, the fawn-colored precipitate thus obtained washed till free from acid, and dried *in vacuo*. A combustion gave the following results : —

0.2290 g. of substance gave 0.5678 g. of $CO_2$ and 0.1312 g. of $H_2O$.

| | Calculated for $C_{14}H_{16}O_4$. | Found. |
|---|---|---|
| Carbon | 67.74 | 67.63 |
| Hydrogen | 6.49 | 6.36 |

*Properties.* It forms a brownish white powder melting in the neighborhood of 100°, but with no definite melting-point; it is insoluble in water, freely soluble in alcohol and glacial acetic acid, slightly in ether, and insoluble in ligroine and benzol. Strong sulphuric acid dissolves it with a reddish-brown color, very different from the purple produced by curcumin. Sodic hydrate dissolves it on warming, and so does sodic carbonate; but the latter solution becomes turbid, and throws down a brownish precipitate on cooling.

The addition of hydrogen to curcumin by sodium amalgam and dilute alcohol is a tedious process occupying more than a week and giving a very bad yield, the product being frequently accompanied by a viscous substance, probably formed by the action of air on the alkaline solution of the hydride. A much better method of adding hydrogen to curcumin consisted in treating it with zinc dust and acetic acid, although in this case the hydride at first produced was further modified in the course of the reaction.

*Anhydride of Curcumin Dihydride,* $(C_{14}H_{15}O_4)_2O$. Curcumin was warmed with acetic acid of 85 per cent and a large quantity of zinc dust, the temperature being kept below the boiling-point of the acetic acid. After some hours the yellow color of the solution had become replaced by a dark brown, and if then a little of the substance gave a yellow instead of a red color with sodic hydrate, the heating was discontinued, and the liquid filtered into water, which precipitated fawn-colored flocks similar to those of the preceding compound. After we had satisfied ourselves that it was impossible to crystallize the substance, we purified it by resolution in glacial acetic acid and precipitation with water; but even this treatment did not remove the whole of the zinc salt, as was shown by the appearance of a slight ash on combustion. This has been subtracted from the weight of the substance taken in calculating the percentages.

The same substance was obtained when curcumin was heated with zinc dust and a solution of ammonic hydrate. The combustion marked III. was of a product made in this way : —

The substance after thorough washing with water was in each case dried on a steam-radiator at a temperature of about 60°.

I. 0.2552 g. of substance gave 0.6460 g. of $CO_2$.
0.1476 g. of $H_2O$. Ash = 0.004.
II. 0.2449 g. of substance gave 0.6183 g. of $CO_2$.
0.1368 g. of $H_2O$. Ash = 0.0061.
III. 0.2357 g. of substance gave 0.6001 g. of $CO_2$.
0.1365 g. of $H_2O$. Ash = 0.002.

| | Calculated for $C_{28}H_{30}O_7$. | Found. | | |
|---|---|---|---|---|
| | | I. | II. | III. |
| Carbon | 70.42 | 70.14* | 70.61* | 70.03* |
| Hydrogen | 6.25 | 6.53 | 6.36 | 6.48 |

*Properties.* It resembles the dihydride closely, like it forming a dirty white powder with no definite melting-point, since it melts gradually in the neighborhood of 120°. The best solvents for it are alcohol and glacial acetic acid, but it is deposited on evaporation of the solvent as a varnish. It is essentially insoluble in ether, ligroine, and benzol, slightly soluble in chloroform. A solution of potassic hydrate dissolves it with a yellow color, while potassic carbonate forms a dark-brown solution if boiled with it, but as this solution cools, brownish flocks are deposited, which we supposed to be a potassium salt, until two analyses of the substance showed that it did not contain more than 2.5 per cent of potassium, whereas the salt with the least possible amount of the metal contains 7.5 per cent. It is evident, therefore, that the potassium was an impurity, which could well be, since we were able to find no satisfactory method of purification. An attempt to make a potassium salt with alcoholic potassic hydrate gave a black liquid, insoluble in a mixture of alcohol and ether, and of the most unpromising appearance.

The fact that the substance forms no salt with potassic carbonate indicates that the two molecules of the dihydride are connected by the removal of water from their carboxyl groups; but we did not consider the nature of the substance satisfactorily explained until we succeeded in making it from the dihydride, $C_{14}H_{16}O_4$, by the action of an acetic-acid solution of zincic acetate. After warming the two substances

* If the ash is not subtracted the percentages are, —

| I. | II. | III. |
|---|---|---|
| 69.04 | 68.85 | 69.44 |
| 6.43 | 6.20 | 6.43 |

together for some time, the product was treated with water, and the precipitate washed, dried, and analyzed, with the following result:—

0.1430 g. of substance gave 0.3666 g. of $CO_2$ and 0.0868 g. of $H_2O$.

| | Calculated for $C_{28}H_{30}O_7$. | Found. |
|---|---|---|
| Carbon | 70.42 | 69.92 |
| Hydrogen | 6.25 | 6.68 |

Whereas before this treatment a portion of the same sample gave carbon 67.63, hydrogen 6.36, as on page 2. This experiment proves, therefore, that the nascent hydrogen given off by zinc dust and acetic acid first converts the curcumin into the dihydride, from which the zincic acetate afterward removes one molecule of water. The anhydride is broken up only incompletely by the action of water at high temperatures or by boiling with sodic hydrate, the product in each case being a mixture of the dihydride and its anhydride.

In order to study the oxidation of the dihydride, some diethylcurcumin, prepared according to the method given in our first paper, was treated with zinc dust and acetic acid. The product thus obtained gave the following results on analysis, which indicate that it is a mixture of di- and monoethylcurcumin dihydride:—

I. 0.2130 g. of substance gave 0.5484 g. of $CO_2$ and 0.1415 g. of $H_2O$. Ash 0.0004.

II. 0.1938 g. of substance gave 0.4986 g. of $CO_2$ and 0.1336 g. of $H_2O$.

| | Calculated for $(C_2H_5)C_{14}H_{15}O_4$. | Found. I. | Found. II. | Calculated for $(C_2H_5)_2C_{14}H_{15}O_4$. |
|---|---|---|---|---|
| Carbon | 69.56 | 70.35 | 70.15 | 71.05 |
| Hydrogen | 7.25 | 7.40 | 7.66 | 7.89 |

Some of this substance was mixed with a saturated neutral solution of potassic permanganate and allowed to stand at the ordinary temperature. The oxidation took place very slowly, several weeks' standing being necessary to complete the reaction. The principal product was proved by its melting-point to be ethylvanillic acid, while the presence of a small quantity of ethylvanillin was indicated by its characteristic smell.

The most striking fact in connection with this reaction was that the dihydride was oxidized with so much more difficulty than curcumin itself.

*Action of Bromine on the Anhydride of Curcumin Dihydride.* When the hydride, dissolved in glacial acetic acid, was mixed with an excess of bromine and allowed to stand over night, the liquid

turned black, and upon addition of water, a red precipitate was thrown down, which was washed with water, dried, and analyzed, —

I. 0.6652 g. of substance gave 0.7160 g. of $CO_2$ and 0.1122 g. of $H_2O$.
0.3100 g. gave according to Carius 0.4125 g. of AgBr.

II. 0.3202 g. gave 0.3498 g. of $CO_2$ and 0.0562 g. of $H_2O$.
0.2786 g. gave 0.3730 g. of AgBr.

| | Calculated for $C_{14}H_{10}Br_4O_4$. | Found. I. | Found. II. |
|---|---|---|---|
| Carbon | 29.89 | 29.36 | 29.80 |
| Hydrogen | 1.78 | 1.87 | 1.95 |
| Bromine | 56.94 | 56.62 | 56.99 |

The substance is red and amorphous; it does not melt under a red heat, but seems to be decomposed without melting. It is insoluble in water, ligroine, and benzol, very slightly soluble in alcohol and ether, soluble in glacial acetic acid. Strong sulphuric acid has no action upon it. It is vigorously acted on by boiling potassic hydrate, forming a red solution, from which acids precipitate a black tarry body which we were unable to purify; two analyses of its sodium salt, however, showed that it contained about the same percentage of oxygen as of carbon, and that most of the bromine (all but 7 per cent) had been removed, proving that the bromine in the original substance is all in the side-chain.

*Action of Bromine on Curcumin.*

We have obtained two bromine compounds of curcumin, one containing four and the other seven atoms of bromine.

*Tetrabromide of Curcumin*, $C_{14}H_{14}Br_4O_4$. When curcumin suspended in carbonic disulphide is allowed to stand with an excess of bromine for some hours, it is converted into a white substance, which is left as the carbonic disulphide evaporates. The carbonic disulphide can be replaced by glacial acetic acid, but in this case an excess of bromine or the use of a large quantity of glacial acetic acid must be avoided. The nature of this body could not be established satisfactorily by analysis, as it was more or less decomposed by all its solvents, and therefore a thorough purification was impossible; we have obtained one fair analysis, however, of a sample washed with carbonic disulphide.

0.2375 g. of substance gave according to Carius 0.3180 g. of AgBr, —

| | Calculated for $C_{14}H_{14}Br_4O_4$. | Found. |
|---|---|---|
| Bromine | 56.66 | 56.99 |

Other specimens contained the following percentages: —

| | | | |
|---|---|---|---|
| Bromine | 54.87 | 58.51 | 58.57 |

To confirm this result, which points to the taking up of four atoms of bromine, we determined the increase of weight caused by the bromine. For this purpose carbonic disulphide and bromine in excess were added to a weighed amount of curcumin, and the product weighed after drying it a little below 100°.

I. 0.252 g. of curcumin gained 0.354 g.
II. 0.218 g. gained 0.300 g.

These results correspond to the following percentages of bromine in the product, —

| | Calculated for $C_{14}H_{14}Br_4O_4$. | Found. I. | Found. II. |
|---|---|---|---|
| Bromine | 56.66 | 58.41 | 57.91 |

And there is therefore no doubt that the substance contains four atoms of bromine. To decide whether it was an addition or substitution product, we determined the amount of hydrobromic acid given off, as in every preparation an evolution of this gas was observed. For this purpose the gases formed in the reaction were allowed to pass through water, and finally the carbonic disulphide and excess of bromine were removed, at first from the curcumin, and afterward from the absorbing water, by a stream of air; the hydrobromic acid collected in the water was then determined as argentic bromide. One gramme of curcumin was used in each case, and in the following comparison of results the amounts found are compared with the calculated amount if the curcumin had given off two molecules of hydrobromic acid, —

| Two Molecules HBr. | I. | II. |
|---|---|---|
| 0.66 | 0.185 | 0.28 |

From this it appears that the hydrobromic acid is produced by an insignificant secondary reaction, and that the substance is an addition product, and therefore has the formula $C_{14}H_{14}Br_4O_4$.* We may add that some experiments to determine directly the number of molecules of bromine added pointed to two molecules as the probable amount, but the results are not definite enough to make them worth publishing.

*Properties.* It is a white or whitish amorphous substance, melting in the neighborhood of 185° with decomposition, but it has no definite

* The high percentages of bromine obtained in the analyses may be accounted for by this secondary reaction.

melting-point. It is insoluble in water, soluble with decomposition in alcohol and in glacial acetic acid, which acts upon it, however, less rapidly than the alcohol, very slightly soluble in ether, chloroform, and carbonic disulphide, insoluble in ligroine and benzol. Its behavior with various reagents was taken up, but no results were obtained which promised to repay further study. The following observations, however, are of some interest. Potassic hydrate and also argentic oxide convert it in part into vanillin, to judge from the smell, while both anilin and zinc cleaned with sulphuric acid act upon it, the former with considerable evolution of heat, — thus confirming the inference that it is an addition-product. The principal products from these reactions, as well as those from the action of sodic carbonate and water, and of reducing-agents, are ill-defined bodies which we could find no means of purifying.

*Pentabromcurcumindibromide*, $C_{14}H_9Br_7O_4$. If curcumin in glacial acetic acid is treated with an excess of bromine, or the solid tetrabromide treated with bromine, a red substance is formed, which, after washing with water and drying *in vacuo*, gave the following results: —

0.2898 g. of substance gave 0.2230 g. of $CO_2$ and 0.0304 g. of $H_2O$.
0.2666 g. of substance gave according to Carius 0.9323 g. of AgBr.

| | Calculated for $C_{14}H_9Br_7O_4$. | Found. |
|---|---|---|
| Carbon | 20.97 | 20.98 |
| Hydrogen | 1.12 | 1.16 |
| Bromine | 69.91 | 69.02 |

*Properties.* A red amorphous substance melting near 120°, but without definite melting-point; insoluble in water, soluble in alcohol apparently with decomposition, easily soluble in ether and glacial acetic acid, leaving a varnish, slightly soluble in benzol, insoluble in ligroine. Strong sulphuric acid acts on it very slowly, finally turning it a more brilliant red. Our study of the behavior of this substance has led to no more definite results than in the case of the tetrabromide.

Heated alone, it gives off bromine and hydrobromic acid, leaving a black tar, from which a yellow substance containing bromine can be extracted by alcohol; we may study this experiment more carefully hereafter. Sodic hydrate, sodic carbonate and water, sodic alcoholate, and argentic oxide all act upon it, but no smell of vanillin was observed in any case. The same is true of several oxidation experiments we have tried upon it, and this would seem to indicate the presence of a portion of the bromine in the benzol ring. It is an

interesting fact that potassic dichromate and sulphuric acid, and also neutral potassic permanganate, attack this substance only with extreme difficulty, whereas they both act vigorously on curcumin.

## SUMMARY.

1. Curcumin takes up two atoms of hydrogen when treated with nascent hydrogen.

2. The dihydride thus formed passes over easily into an anhydride by losing one molecule of water.

3. The anhydride of diethylcurcumin dihydride is much less easily attacked by oxidizing agents than diethylcurcumin, but the products are the same, — ethylvanillic acid with a trace of ethylvanillin.

4. Bromine removes two atoms of hydrogen from the dihydride, and replaces four more, forming $C_{14}H_{10}Br_4O_4$.

5. Only four atoms of bromine can be added to curcumin.

6. The tetrabromide has a great tendency to form vanillin when treated with substances which remove bromine.

7. With an excess of bromine a substance, $C_{14}H_9Br_7O_4$, is formed.

8. The pentabromcurcumindibromide is oxidized in neutral or acid solutions only with great difficulty.

The observations just described throw some light upon the nature of the side-chain of curcumin, but as the inferences to be drawn from them are at best extremely doubtful, we shall postpone all discussion of the structure of curcumin until our further study of it has put the subject on a more secure basis.

## III. TURMERIC OIL — TURMEROL.

The oil obtained from turmeric, which amounts to about 11 per cent of its whole weight, has naturally attracted the attention of chemists much less than curcumin, the yellow coloring-matter of the root; we find consequently only a few analyses and some meagre statements about the action of reagents upon the oil, in place of the much fuller study to which curcumin had been submitted. The most important of these will be found in the papers of Ivanow-Gajewsky * and Kachler,† but as they all refer to mixtures, it is not necessary to repeat them here. The oil, however, is not without practical interest, as to it the turmeric (and therefore curry powder) owes its aromatic taste and smell.

* Ber. d. ch. G. 172, p. 1103.

† Ber. d. ch. G. 170, p. 713.

The crude product with which we started in the following study of the oil was extracted, from ground Bengal turmeric with ligroine, in the way already described in the first paper * of this series. After being freed from the higher boiling portions of the ligroine by heating to 150° in a boiling-flask, it formed a rather thick oily liquid, with a yellow color, and pleasant aromatic smell. The purification offered some difficulty, because it was decomposed by distillation under ordinary pressure, giving distillates with a rank, disagreeable smell; and distillation with steam, although effecting a partial purification, was an extremely tedious process, owing to the difficulty with which the oil was driven over. We were therefore obliged to resort to fractional distillation under diminished pressure, and in this way at last succeeded in separating the oil into three fractions, — the first, boiling below 193° under 60 mm. of pressure; the second, from 193°–198°; and the third, the retort residue, a viscous, semi-solid body of extremely uninviting appearance. We have up to this time confined our attention to the middle fraction, although a few experiments on the fraction below 193° would indicate that it consists of the middle fraction contaminated with hydrocarbons from the ligroine used in the extraction of the oil, — a view which is borne out by the very small amount of this fraction. For the fraction from 193°–198°, which is the subject of this paper, we would propose the name *turmerol.*

*Composition of Turmerol.*

I. 0.1924 g. of the oil gave 0.5903 g. of $CO_2$ and 0.1814 g. of $H_2O$.
II. 0.3126 g. gave 0.9588 g. of $CO_2$ and 0.3010 g. of $H_2O$.
III. 0.2354 g. gave 0.7157 g. of $CO_2$ and 0.2190 g. of $H_2O$.
IV. 0.2002 g. gave 0.6123 g. of $CO_2$ and 0.1818 g. of $H_2O$.
V. 0.2448 g. gave 0.7492 g. of $CO_2$ and 0.2306 g. of $H_2O$.

| | I. | II. | III. | IV. | V. | Mean. |
|---|---|---|---|---|---|---|
| Carbon | 83.68 | 83.66 | 82.90 | 83.43 | 83.47 | 83.62 |
| Hydrogen | 10.47 | 10.70 | 10.34 | 10.10 | 10.47 | 10.42 |

I.–III. are analyses of the same sample; IV. and V. analyses of a different sample. To test the purity of the oil, the original sample was distilled again *in vacuo*, and collected in three equal fractions. Of the analyses which follow, VI. was made with the portion which came over first; VII. and VIII. with that which came over last.

* These Proceedings, Vol. XVII. p. 110.

VI. 0.3315 g. gave 1.0194 g. of $CO_2$ and 0.3145 g. of $H_2O$.
VII. 0.2837 g. gave 0.8675 g. of $CO_2$ and 0.2604 g. of $H_2O$.
VIII. 0.2706 g. gave 0.8228 g. of $CO_2$ and 0.2474 g. of $H_2O$.

| | Lower Fraction. | Higher Fractions. | |
|---|---|---|---|
| | VI. | VII. | VIII. |
| Carbon | 83.86 | 83.39 | 82.92 |
| Hydrogen | 10.54 | 10.20 | 10.16 |

From this it appears that the substance is essentially pure and homogeneous.

As has been stated already, the turmerol can be purified to a certain extent by distillation with steam ; analysis IX. was made with a sample prepared in this way, while X. was made with some of the same sample after it had been distilled once under ordinary pressure. These specimens were extracted with carbonic disulphide instead of ligroine.

IX. 0.2260 g. gave 0.6860 g. of $CO_2$ and 0.2195 g. of $H_2O$.
X. 0.2636 g. gave 0.8038 g. of $CO_2$ and 0.2546 g. of $H_2O$.

| | IX. | X. |
|---|---|---|
| Carbon | 82.78 | 83.16 |
| Hydrogen | 10.77 | 10.73 |

The analyses unfortunately are not capable of establishing the formula of turmerol with certainty, since the difference between the members of the homologous series is very small, as is shown by the following comparison: —

| | Mean of the Preceding Analyses. | $C_{18}H_{26}O$. | $C_{19}H_{28}O$. | $C_{20}H_{30}O$. |
|---|---|---|---|---|
| Carbon | 83.62 | 83.73 | 83.81 | 83.90 |
| Hydrogen | 10.42 | 10.08 | 10.29 | 10.49 |

Taking both the hydrogen and the carbon into consideration, our results agree best with the formula $C_{19}H_{28}O$, as shown above in the case of the mean, and a comparison of the separate analyses with the calculated percentages also declares in favor of this formula. But it is evident that it is impossible to decide definitely from these data in favor of this formula, nor can the derivatives we have prepared from the oil settle this question, as a thorough purification of these bodies has proved impossible on account of their ill-defined properties and slight stability.

We are inclined to ascribe the differences between analyses VI. and VII. and VIII. to the presence of a trace of some hydrocarbon from the ligroine, but did not attempt to purify the substance further, as it is slightly decomposed, even by distillation, under a pressure of 60 mm.

*Properties of Turmerol.*

The substance analyzed by us had a pale yellow color, an agreeable, not very strong aromatic smell, and a specific gravity of 0.9016 at 17°. It turns a ray of polarized light to the right with the following specific rotary power for sodium light: —

$$[\alpha] = 33.52.$$

Under ordinary pressure it boils at 285°–290°, but decomposes apparently with formation of water, giving a substance with a lower boiling-point. At a pressure of 60 mm. it boils from 193° – 198°, but even under this pressure suffers a slight decomposition. It is essentially insoluble in water, but mixes easily with all other common solvents. Acid sodic sulphite in aqueous solution has no action upon it.

In order to determine the nature of turmerol, its behavior with various reagents was next studied.

*Action of Hydrochloric Acid. Turmerylchloride.*

When turmerol was heated with aqueous hydrochloric acid saturated at 0° to 150° in a sealed tube for some hours, a brown oily liquid was formed having a different smell from the original substance, which, when washed until free from acid and dried *in vacuo*, gave the following results on analysis: —

I. 0.2938 g. of substance gave 0.8464 g. of $CO_2$ and 0.2530 g. of $H_2O$.

0.4434 g. of substance gave according to Carius 0.2190 g. of AgCl.

II. 0.3179 g. of substance gave 0.1518 g. of AgCl.

| | Calculated for $C_{19}H_{27}Cl$. | Found. I. | II. |
|---|---|---|---|
| Carbon | 78.48 | 78.57 | |
| Hydrogen | 9.30 | 9.57 | |
| Chloride | 12.22 | 12.21 | 11.80 |
| | 100.00 | 100.35 | |

Analyses I. and II. were made with specimens from different preparations. The substance was a pale brownish oil with an agreeable smell, different from that of turmerol; it decomposed on distillation, and also lost chlorine when distilled with steam or even with fuming hydrochloric acid.

The same compound was formed by the action of phosphorous

trichloride on turmerol, but much less neatly. Phosphoric pentachloride, on the other hand, seemed to add chlorine also, as the product from its action on turmerol contained about 15 per cent of chlorine. We have postponed the study of this substance for the present.

The formation of the turmerylchloride described above indicates that turmerol is an alcohol, and to confirm this view we next treated the turmerylchloride with various reagents, and found that its chlorine was removed, in part, at least, by boiling water or by alcoholic solutions of sodic acetate, potassic cyanide, or ammonia, — a substance being formed in each case with the characteristic smell of the class to which it should belong. The regenerated alcohol and the acetate we were unable to purify, while the nitrile and its corresponding acid and the amine were formed in very small quantities and did not give crystalline compounds, so that their further study, which we had at first hoped would establish the formula of turmerol, did not promise to repay the labor.

To still further confirm the alcoholic nature of turmerol, we prepared the sodium compound as follows, —

*Action of Sodium on Turmerol.*

Some of the turmerol mixed with high boiling ligroine was warmed with sodium in a flask with a return cooler for twelve hours, during which time hydrogen was given off; the liquid was then filtered, and the ligroine evaporated off from the viscous filtrate.

I. 0.1456 g. of substance gave 0.0374 g. of $Na_2SO_4$.
II. 0.9820 g. gave 0.2342 g. of $Na_2SO_4$.

| | Calculated for $C_{19}H_{27}ONa$. | Found. I. | Found. II. |
|---|---|---|---|
| Sodium | 7.82 | 8.32 | 7.72 |

The substance forms a viscous semi-solid mass.

Sodic hydrate seemed not to act upon turmerol.

An attempt to convert turmerol into its acetate by heating it with acetic anhydride and sodic acetate on the water-bath gave a product having the same smell as that from the reaction of sodic acetate on turmerylchloride, but no means could be found of separating it from the unaltered turmerol, as it was decomposed by distillation even *in vacuo*. We accordingly turned our attention to the ethers of turmerol, and selected for study the isobutylether, as the difference between the percentage composition of this and that of the alcohol would be greater than in the case of the methyl- or ethylethers.

### *Isobutylether of Turmerol.*

This body was prepared by boiling the sodium compound with isobutyliodide in a flask with a return-condenser for some time; the product was purified by distillation *in vacuo.*

I. 0.2110 g. of substance gave 0.6524 g. of $CO_2$ and 0.2039 g. of $H_2O$.

II. 0.2742 g. of substance gave 0.8520 g. of $CO_2$ and 0.2646 g. of $H_2O$.

| | Calculated for $C_{10}H_{17}OC_4H_9$. | Found. I. | II. |
|---|---|---|---|
| Carbon | 84.14 | 84.45 | 84.71 |
| Hydrogen | 10.97 | 10.73 | 10.83 |

It is a heavy yellowish oil with a pleasant smell. The ethylether is a similar substance.

From the observations described there can be no doubt that turmerol is an alcohol.

### *Oxidation of Turmerol.*

When turmerol was treated with a hot aqueous solution of potassic permanganate until it was no longer decolorized, and after destroying the slight excess of permanganate with sodic sulphite the liquid was filtered from the brown hydrate of manganese, upon adding sulphuric acid a yellowish-white precipitate was thrown down, which, purified by washing with alcohol, became perfectly white, and volatilized without melting, indicating that it was terephthalic acid. To prove that this was the case, the acid was converted into the methylester by passing hydrochloric acid through methylalcohol, in which it was suspended. The solid gradually dissolved, and upon allowing the alcohol to evaporate, long prisms were deposited, which, after two crystallizations from hot alcohol, melted at 139°–140°. Melting-point of methylester of terephthalic acid 140°. Another sample of the acid was analyzed,—

0.1782 g. of substance gave 0.3798 g. of $CO_2$ and 0.0641 of $H_2O$.

| | Calculated for $C_8H_6O_4$. | Found. |
|---|---|---|
| Carbon | 57.83 | 58.12 |
| Hydrogen | 3.62 | 4.00 |

The product in this case, therefore, is terephthalic acid, and turmerol must stand in close relationship to the para series of aromatic compounds. It is probably a derivative of the terpenes.

The formation of terephthalic acid from turmeric oil also explains

the results of Ivanow-Gajewsky in regard to the oxidation of curcumin, as it renders it almost certain that the terephthalic acid obtained by him, but of which we could find no trace, proceeded from an impurity of turmeric oil in his curcumin.

When cold potassic permanganate not in excess is used, turmerol yields one or more apparently new acids, with the investigation of which we are at present occupied.

### Summary.

The formula of turmerol (the fraction of turmeric oil boiling from 193° to 198° under 60 mm. of pressure) is $C_{19}H_{28}O$, or one of its adjacent homologues.

Its alcoholic nature is proved by the following observations: —

1. Conversion into $C_{19}H_{27}Cl$ by hydrochloric acid or phosphorous trichloride. The chlorine can be removed by ordinary reagents.

2. The formation of a compound, $C_{19}H_{27}ONa$, by the action of sodium.

3. The formation of its isobutylether, $C_{19}H_{27}OC_4H_9$.

That it is related to the para compounds of the aromatic series is proved by its conversion into terephthalic acid by treatment with a hot aqueous solution of potassic permanganate in excess.